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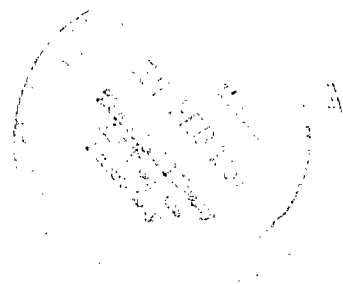
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IONIC CONDUCTIVITY OF CALCIUM AND STRONTIUM FLUORIDES

by William L. Fielder
Lewis Research Center
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SUMMARY

The conductivities of single crystals of calcium and strontium fluoride were determined. In the extrinsic region (impurity controlled), the specific conductivity of each crystal may differ. The extrinsic conductivities K_I for the normal process of point-defect migration for two calcium fluoride (CaF_2) crystals (A and B) between 430° and 535° C were as follows (in $\text{ohm}^{-1} \text{cm}^{-1}$): for A, $K_I = 1.11 \pm 0.01 \times 10^{-1} \exp - (16\,500 \pm 100/RT)$ and for B, $K_I = 1.21 \pm 0.01 \times 10^{-1} \exp - (16\,500 \pm 100/RT)$ where R is the gas constant (cal/(deg)(mole)) and T is the absolute temperature (deg). The extrinsic conductivity of strontium fluoride (SrF_2) between 360° and 410° C was $K_I = 1.22 \pm 0.05 \times 10^{-2} \exp - (17\,400 \pm 900/RT)$.

Only one intrinsic region was observed for two calcium fluoride crystals between 645° and 830° C or for strontium fluoride between 580° and 760° C. The intrinsic conductivities K_P were as follows (in $\text{ohm}^{-1} \text{cm}^{-1}$): for CaF_2 , $K_P = 4.08 \pm 0.10 \times 10^6 \exp - (46\,500 \pm 200/RT)$ and for SrF_2 , $K_P = 6.6 \pm 0.2 \times 10^5 \exp - (43\,100 \pm 200/RT)$. The thermally produced defects, responsible for the conductivity of these fluorides in the intrinsic region, are suggested to be fluorine ion vacancies.

Finally, activation energy requirements were related to the energies of migration and formation. The primary mechanisms consistent with the results are the formation and migration of fluorine ion vacancies. For the intrinsic region, fluorine ion vacancies in calcium and strontium fluorides are formed thermally with a formation energy of 60.0 and 51 kilocalories, respectively, for the Frenkel pair. For the extrinsic region, these vacancies are formed, predominantly, by means of monovalent impurities. Migration of these vacancies in the fluorides of calcium and strontium occurs with energies of 16.5 and 17.4 kilocalories, respectively.

INTRODUCTION

When solids are classified as being metallic, semiconductors, or insulators, the inference is that conduction occurs only by means of electrons. However, certain ionic solids conduct partially or completely by means of an ionic mechanism. This has been shown to be the case for the strongly ionic halides of group I (alkali metal group) (ref. 1) and group I (B) (copper and silver) (ref. 2). Although considerable information is available concerning the simpler structured alkali metal halides, less is known for other strongly ionic solids. The group II fluorides (calcium, strontium, and barium) are of special interest since they are strongly ionic, divalent, and structurally more complex. Furthermore, these fluorides are relatively stable, less deliquescent, and less reactive than the other halides of group II. Conductivities of single crystals of barium fluoride were reported previously (ref. 3). For a more detailed understanding of the mechanisms for the conductivities of the group II halides, it was necessary to study the fluorides of strontium and calcium, which are also of the fluorite crystal structure.

The conductivity of strontium fluoride has been reported and activation energies have been suggested (ref. 4). However, better accuracy in conductivity data should result by using single crystal specimens which lack large amounts of monovalent or trivalent impurities.

The conductivity of calcium fluoride has also been reported (ref. 5). The primary objective of that investigation was to observe the influence of impurities on the conductivity of calcium fluoride. Although this investigation was quite informative, several questions still remained unanswered. For example, the energy requirements (activation energy and preexponential factor) for calcium fluoride, containing sodium fluoride, for the extrinsic region varied considerably with temperature. In addition, conflicting values for the energy requirements were obtained for this region. In order to determine the energy requirements more accurately, it was necessary to redetermine the conductivity of calcium fluoride.

The energy requirements were obtained from the data and compared with the two previous investigations. Finally, some mechanisms which were consistent with the data were suggested for the ionic conductivity of the fluorides of calcium and strontium.

SYMBOLS

A	crystal area, sq cm
A_I	preexponential factor for region controlled by impurities, $\text{ohm}^{-1} \text{ cm}^{-1}$
A_P	preexponential factor for pure material, $\text{ohm}^{-1} \text{ cm}^{-1}$

A_S	preexponential factor along planar or line imperfection, $\text{ohm}^{-1} \text{cm}^{-1}$
E_F	formation energy of fluorine ion vacancy and fluorine ion interstitial, cal/mole
E_I	activation energy for region controlled by impurities, cal/mole
E_{MV}	migration energy of the fluorine ion vacancy, cal/mole
E_P	activation energy for pure material, cal/mole
E_S	migration energy along planar or line imperfection, cal/mole
K	observed specific conductivity, $\text{ohm}^{-1} \text{cm}^{-1}$
K_I	specific conductivity for region controlled by impurities, $\text{ohm}^{-1} \text{cm}^{-1}$
K_P	specific conductivity for pure material, $\text{ohm}^{-1} \text{cm}^{-1}$
L	crystal length, cm
R	gas constant, cal/deg-mole
R_S	specific resistance, ohm-cm
R_T	total resistance, ohm
T	absolute temperature, deg

EXPERIMENTAL

Single crystals of calcium and strontium fluorides were obtained commercially. Spark-source mass-spectrometric analyses of both fluorides are given in table I. These crystals, which had been prepared in a manner similar to the Stockberger technique, were obtained as cubes of about 1.3 by 1.3 by 1.3 centimeters. Surface irregularities were removed by grinding and polishing the crystals with methanol on fine emery paper and polishing cloths. Most of the crystal manipulations were performed under flowing nitrogen gas to minimize the adsorption of water. After polishing, the crystals were colorless, transparent, and contained no internal flaws which were visible to the eye. Three planes were used for the calcium fluoride crystal faces in an attempt to determine whether crystal orientation might influence the conductivity. Crystal A had 111 planes for the two faces and 110 planes for the sides. Crystal B had 110 planes for the two faces and 110 and 100 planes for its sides. Crystal C had 100 planes for its faces and sides.

Two methods of coating the surfaces of the crystal faces were used to minimize polarization effects. One coating consisted of several thin coats of an emulsion of colloidal graphite in isopropyl alcohol.¹ The alcohol was then removed in vacuum at higher

¹Dag dispersion number 154.

temperatures. Most measurements, however, were made on crystals which had platinum sputtered on their faces in the absence of air or oxygen.

Essentially, the same apparatus and procedure which had been used for barium fluoride (ref. 3) were used for controlling and measuring the temperatures of these crystals. The crystals were heated in a three-zone furnace. Each zone was controlled by means of a saturable-core-reactor proportional control unit. The crystals were usually preheated to 250° to 400° C in vacuum to remove oxygen, adsorbed water, and other gaseous impurities; then, they were cooled to room temperature. Helium gas, which had been purified by passage over copper chips at 375° C and through a liquid-nitrogen trap, was introduced into the system to a pressure of about 400 torr. Temperatures were determined by means of calibrated platinum-platinum 13-percent rhodium thermocouples. For most of the measurements, the temperatures of both platinum electrodes were observed. These two temperatures usually did not differ by more than 0.2 to 0.4° C, and the temperature of the crystal was taken as the average of these readings.

The same apparatus and methods (ac and dc) which had been used previously were also used to measure the resistances of these crystals. The direct-current electrometer method was used only for strontium fluoride in the resistance range of about 10⁷ to 10⁶ ohms. The particular alternating-current method used does not give reliable data for this range. Most of the resistance measurements were made at frequencies of 100 cps, 1 kcps, and 10 kcps with an impedance comparator bridge and standard resistors. A small polarization effect was always observed for both calcium and strontium fluorides for either the platinum or graphite surface coatings and was indicated by a slight increase in the crystal resistance when the frequency was decreased. This effect was small (about 0.6 percent) and was not considered further.

Since the crystal dimensions do not remain constant with temperature, the necessary corrections for thermal expansion were made.

RESULTS AND DISCUSSION

General Discussion of Ionic Conductivity

The ionic conductivity for single crystals can be obtained from resistance measurements as follows:

$$K = \frac{1}{R_S} = \left(\frac{L}{R_T A} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1} \quad (1)$$

where K is the observed specific conductivity ($\text{ohm}^{-1} \text{ cm}^{-1}$), R_S is the specific

resistance (ohm-cm), R_T is the total resistance (ohm), A is the crystal area (sq cm), and L is the length (cm).

Both strontium and calcium fluorides conduct by means of ions rather than by electrons. Ion migrations may occur either by an ion interchange or by means of imperfections in the crystal. The process of ion interchange will not be considered further since the energy requirements would be too high. Three types of crystal imperfections may exist: (1) planar (e.g., grain boundaries); (2) line (e.g., dislocations); and (3) point (e.g., fluorine ion interstitials or vacancies or cation interstitials or vacancies). While planar and line imperfections may be of some importance in polycrystalline materials, they are usually assumed to make only minor contributions to the conductivity in well-annealed, single crystals.

Transport studies have shown that the most probable migrating species in barium fluoride is the fluoride ion (ref. 6). Similarly, it was suggested that the transport of calcium ions in calcium fluoride, as shown by diffusion measurements, is almost nonexistent. The transport number is about 10^{-6} at 1000°C (ref. 5). These transference number experiments seemed to indicate that point-defect mechanisms which involve the transfer of calcium ions (in CaF_2) or strontium ions (in SrF_2) would be of minor importance. Therefore, although the mechanism involving the movement of both positive ions and fluorine ions to the surface and the formation of vacancies cannot be rejected categorically, it seems unlikely that it will contribute significantly to the conductivity at moderate temperatures. Of primary importance, however, are those defects, such as fluorine ion vacancies and fluorine ion interstitials, which lead to conductivity by means of the fluorine ions.

In an "absolutely pure" calcium or strontium fluoride crystal, the mechanism involves the thermal movement of a normal fluorine ion from its lattice site into an interstitial position, leaving a fluorine ion vacancy site (fig. 1(b)):

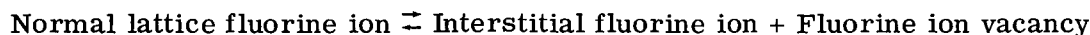


Figure 1 is only a simple planar representation, however, and is not truly indicative of the fluorite structure of the two fluorides. Fluorine ions can migrate through the crystal by moving either to different interstitial positions or through the vacancies. Whether the migration of one of these defects will dominate the conductivity will depend upon the energy requirements involved. If the energy requirements for the migration of the interstitial fluorine ions are much larger than for the fluorine ion vacancies, the general equation for the conductivities (by vacancy point defects) of the pure fluorides is (ref. 7)

$$K_P = A_P \exp - \left(\frac{E_P}{RT} \right) \quad (2)$$

where K_P is the specific conductivity for the pure material ($\text{ohm}^{-1} \text{ cm}^{-1}$), A_P is its preexponential factor ($\text{ohm}^{-1} \text{ cm}^{-1}$), E_P is the activation energy (cal/mole), R is the gas constant (cal/mole-deg), and T is the absolute temperature (deg). The activation energy is simply (ref. 7)

$$E_P = \frac{E_F}{2} + E_{MV} \quad (3)$$

where E_F is the formation energy of the two defects (cal/mole) and E_{MV} is the migration energy of the fluorine ion vacancy (cal/mole).

If the log of the specific conductivity is plotted against the reciprocal of the absolute temperature, two distinct regions are usually obtained: (1) an extrinsic region for the lower temperatures and (2) an intrinsic region for the higher temperatures. Examples are shown in figure 2. For the impurity-controlled region (extrinsic), the quantity of one of these defects is essentially constant with temperature, since the number of defects produced by impurities is much larger than the number which is produced thermally. For example, as shown in figure 1(c), a monovalent fluoride impurity (NaF) will produce only fluorine ion vacancies. If the energy requirements for the migration of these vacancies are smaller than for fluorine ion interstitials, the impurity region conductivities are

$$K_I = A_I \exp - \left(\frac{E_I}{RT} \right) \quad (4)$$

where K_I is the specific conductivity for the region completely controlled by the impurities ($\text{ohm}^{-1} \text{ cm}^{-1}$), A_I is its preexponential factor ($\text{ohm}^{-1} \text{ cm}^{-1}$), and E_I is the activation energy for this region (cal/mole). For this case, the activation energy is also equal to the migration energy of the fluorine ion vacancies.

The observed specific conductivity at any temperature will depend, therefore, on the contributions of both of these regions. It has been suggested that the observed specific conductivity K can be expressed as follows (ref. 8)

$$K = \frac{(K_P)^2}{(K - K_I)} \quad (5)$$

In order to calculate the conductivities of a crystal as a pure material K_P and of the region which is completely controlled by impurities K_I , the following procedure was used. First, the observed conductivity for the upper temperature region was assumed to represent that for the pure material K_P . The straight line plot of $\log K$ against the reciprocal of the temperature for this upper region was extrapolated to the lower tem-

perature region to represent K_P at the lower temperatures. The preliminary values of K_I were calculated from the observed data by means of equation (5). Second, the preliminary values for the pure material were then calculated from the data observed for the upper temperature region and the K_I values which were extrapolated to the upper region in the same manner as for K_P . Two repetitions of this procedure were usually more than adequate for determining the final K_P and K_I values.

The derivation of equation (2) had also assumed that only point defects were contributing to the conductivity. Under certain conditions, planar or line imperfections may also contribute to the conductivity. A more general expression for equation (2) should be

$$K_P = A_P \exp - \left(\frac{E_P}{RT} \right) + A_S \exp - \left(\frac{E_S}{RT} \right) \quad (6)$$

where A_S is the preexponential factor for this region ($\text{ohm}^{-1} \text{ cm}^{-1}$) and E_S is the migration energy along planar or line imperfections (cal/mole). Similarly, the impurity controlled region should be

$$K_I = A_I \exp - \left(\frac{E_I}{RT} \right) + A_S \exp - \left(\frac{E_S}{RT} \right)$$

In general, however, the second term is ignored in well-annealed, single crystals since its contribution should be small.

Results for Strontium Fluoride

Both regions were obtained for the strontium fluoride crystal. The extrinsic region, resulting from direct-current measurements between 360° and 410° C, is shown in figure 3. First, the log of the observed specific conductivities K was plotted against the reciprocal of the absolute temperature. Second, the extrinsic specific conductivities K_I were calculated, as suggested by equation (5) and shown in figure 3.

The activation energies were determined from the slopes. The standard deviations were determined for the calculated extrinsic conductivities K_I . The activation energy and the preexponential factor are shown in table II. The conductivities for the strontium fluoride crystal, for this region, can be expressed by the following equation:

$$K_I = 1.22 \pm 0.05 \times 10^{-2} \exp - \left(\frac{17\,400 \pm 900}{RT} \right)$$

Only one intrinsic region was observed for strontium fluoride between 580° and 760° C. The observed specific conductivities K are shown in figure 4. In addition, the conductivities which eliminated the contributions of the impurity region K_P were calculated. The activation energies, preexponential factors, and standard deviations were calculated and are given in table III. The specific conductivities of "absolutely pure" strontium fluoride can be expressed by the following equation:

$$K_P = 6.6 \pm 0.2 \times 10^5 \exp - \left(\frac{43,100 \pm 200}{RT} \right)$$

Croatto had observed the conductivities of pressed powders of strontium fluoride between 400° and 1100° C (ref. 4). Although these pellets usually contained lanthanum fluoride as impurities, it was suggested that "pure" strontium fluoride gave only one region with an activation energy of 31.8 kilocalories. Croatto's data differed considerably from the aforementioned equation and, apparently, did not represent the same mechanism.

Results for Calcium Fluoride

The extrinsic conductivities for three crystals of calcium fluoride were obtained between 430° and 535° C. These conductivities were corrected to eliminate the intrinsic contribution. The resulting conductivities K_I are shown in figure 5. The activation energies, preexponential factors, and standard deviations are given in table II. Crystal A (111 face) and crystal B (110 face) gave, essentially, the same conductivities and the same value of 16.5 kilocalories for the activation energy. However, crystal C (100 face) gave a value of about 12.1 kilocalories. Subsequent studies seemed to indicate that this difference in energies was not due to a preferred planar conductivity for the crystal with the 100 face. Crystal A, after heating to moderately high temperatures and cooling relatively rapidly, was turned over to its side, as crystal A', so that its 110 plane became its face. An energy of about 11.8 kilocalories was observed in crystal A'. Finally, two competing processes were found to be responsible for this extrinsic conductivity. Crystal A' (110 face) was returned to its original 111 plane, as crystal A'', after heating to high temperatures and cooling more slowly. If a preferred plane of conductivity had existed, the conductivity should have returned to its original values of crystal A. Instead, two values were found: (1) an energy of about 13 kilocalories (similar to crystals A' and C) between 430° and 470° C and (2) an energy of about 17 kilocalories (similar to A and B) between 470° and 555° C. Thus, while the extrinsic conductivity generally occurs with an energy of about 16.5 kilocalories (SrF_2 was about 17 kcal), a competing process with an energy of about 12 kilocalories may occur particularly at the lower temperatures

of the extrinsic region.

The specific conductivities for the impurity region of calcium fluoride single crystals A and B can be represented by the following equations:

$$K_I = 1.11 \pm 0.01 \times 10^{-1} \exp - \left(\frac{16\,500 \pm 100}{RT} \right)$$

$$K_I = 1.21 \pm 0.01 \times 10^{-1} \exp - \left(\frac{16\,500 \pm 100}{RT} \right)$$

It is of interest to compare these values with the values obtained by Ure for doped calcium fluoride crystals (ref. 5). The addition of yttrium fluoride, which produces interstitial fluorine ions (and some positive ion vacancies), as shown in figure 1(d), leads to activation energies of about 27 kilocalories. However, doping with sodium fluoride, which produces fluorine ion vacancies, leads to values lower than 27 kilocalories. For example, Ure suggested that most of the monovalent doped crystals had activation energies ranging between 14 and 18 kilocalories for 300° to 550° C. One crystal, however, had an energy of about 12 kilocalories, suggesting that a lower energy process may also occur.

Only one intrinsic region was obtained for crystals A and B between 645° and 830° C, as shown in figure 6. However, two regions were observed for crystal C. As suggested previously, the conductivity of crystal C probably contained a lower energy competing process in addition to the normal impurity controlled process in this extrinsic region. Therefore, these extrinsic values should be subtracted from the intrinsic values in order to determine the conductivity of crystal C which is due to the migration of point defects uniformly throughout the crystal. Then, as shown in figure 6, crystal C' gave only one line which was almost identical to the observed conductivities for crystals A and B. The activation energies, from these observed conductivities, for crystals A, B, C, and C', are given in table III. The values for A, B, and C' range from 44.8±0.2 to 45.5±0.1 kilocalories. This range of energies suggests that a preferred plane of conductivity cannot be rejected categorically. However, since these differences are still relatively small and almost the same as the limit of error, it was assumed that all planes are of equal conductivity.

The activation energies calculated for "absolutely pure" crystals of A and B (from K_p) are also given in table III. For this region, the specific conductivity should not depend on the purity or past history of the crystals if the same mechanism is occurring. All similar crystals should give, essentially, the same conductivities. The best overall activation energy of 46.5 kilocalories was assumed for calcium fluoride, and the preexponential factors were calculated. The specific conductivities of "absolutely pure"

calcium fluoride can be expressed by the following equation:

$$K_P = 4.08 \pm 0.10 \times 10^6 \exp - \left(\frac{46\,500 \pm 200}{RT} \right)$$

This agrees reasonably well with the following equation suggested by Ure (ref. 5):

$$K = 2.2 \pm 0.2 \times 10^6 \exp - \left(\frac{44\,800 \pm 600}{RT} \right)$$

Suggested Mechanisms for Calcium and Strontium Fluorides

The following activation energies for the conduction process in the extrinsic regions were obtained in the present investigation: (1) both calcium fluoride crystals (A and B) gave values of 16.5 kilocalories and (2) strontium fluoride gave a value of 17.4 kilocalories. In previous investigations, the addition of yttrium fluoride to calcium fluoride (which introduces fluorine ion interstitials) led to energies greater than 27 kilocalories, and, the addition of sodium fluoride to calcium fluoride (which introduces fluorine ion vacancies) gave values ranging from 12 to 18 kilocalories (ref. 5). It seems probable that these values of 12 to 18 kilocalories, for calcium fluoride doped with sodium fluoride, represent the migration energy of fluorine ion vacancies. Therefore, the observed values of 16.5 and 17.4 kilocalories for the intrinsic conductivity of pure calcium and strontium fluorides, respectively, undoubtedly represent the migration of fluorine ion vacancies uniformly throughout the crystal.

Calcium fluoride crystal C gave an extrinsic activation energy of only 12.1 kilocalories. This lower energy for crystal C indicated that a competing mechanism was occurring. Furthermore, a competing process (11.8 kcal) became significant for crystal A, as A', after cooling fairly rapidly from moderately high temperatures. Finally, crystal A, as A'', showed both competing processes quite clearly by giving both activation energies (13 and 17 kcal). This lower energy was not due to conduction throughout the crystal along a preferred plane of orientation, since crystal A had a 111 face while A' and A'' had 110 and 111 faces, respectively. Nor was this lower energy due to electronic conduction throughout the crystal. The band gap in these fluorides should be too high for electronic conduction and transference numbers had indicated that only ions were migrating.

It is possible that some other chemical species, in addition to the fluorine ions, are contributing to the conductivity, and, thereby, leading to these lower energies. Both fluorides were of moderate purity. The major impurities in both crystals were other

group II fluorides which would not significantly change the conductivity. Although the crystals were surrounded by purified helium, it is conceivable that traces of oxygen or water vapor might react with calcium fluoride to form traces of ions, such as oxides. However, it is believed that migration of oxide ions is not responsible for this lower energy, since the migration energy of the oxide ion in aluminum oxide is about 60 kilocalories (ref. 9). Therefore, although the migration of some other chemical species cannot be rejected categorically, it seems unlikely for pure crystals.

A possible explanation for the lower energy would be that fluorine ions migrate along easier paths in the crystal, such as planar or line imperfections, since for single crystals, under certain conditions, some conductivity due to planar or line imperfections should be expected. For example, grain boundaries are known to increase the conductivity of pressed powders of silver bromide (ref. 10). Further, a certain number of planar or line imperfections will always be present, particularly if the crystals are cooled too rapidly. A reasonable amount of annealing will not always eliminate completely all of these imperfections. For example, annealing of lithium fluoride at 800° C for 16 hours decreased the number of dislocations at the surface, but the interior remained essentially unchanged (ref. 11). In fact, annealing of calcium fluoride in the presence of impurities could even contribute to the formation of dislocations. For example, water vapor (or oxygen) will react with calcium fluoride at high temperatures to produce calcium oxide and hydrogen fluoride (or fluorine). It is also conceivable that traces of oxides within the crystal may react similarly to form calcium oxide and fluorine. It has been suggested that introduction of this oxide ion into the lattice may cause enough lattice strain to generate dislocations (ref. 12). If sufficient planar or line imperfections are present, migration along these paths should occur more easily with lower energies. As an example, the energy of activation for self-diffusion in silver along these imperfections is about 20 kilocalories per mole, compared to 46 kilocalories per mole in the normal lattice (ref. 13). For silver bromide, the energy of migration for silver ions in a deformed single crystal was only about 5.8 kilocalories, compared to about 10 kilocalories in the annealed, single crystal (ref. 14). These lower energies may be of particular significance for the lower temperatures of the extrinsic region, since the point defects are attracted to these imperfections. For instance, when a divalent halide is added to sodium chloride in small amounts, the vacancies so produced are attracted strongly to the dislocation lines (ref. 15).

Under certain conditions, therefore, a smaller number of fluorine ion vacancies in calcium fluoride (and probably in strontium fluoride) may migrate along easier paths (e. g., dislocations or grain boundaries) and control the conduction process, particularly for the lower temperatures of the extrinsic region. The normal process of migration of fluorine ion vacancies throughout the crystal is then expected to become increasingly

more important and to control the process for the higher temperatures of the extrinsic region.

Calcium fluoride crystals A and B gave only one intrinsic region; however, crystal C gave two regions (41.6 and 44.5 kcal). Crystal C was the one which contained an additional conductivity contribution caused by the lower energy process, as indicated in equation (6). Therefore, the intrinsic conductivity of crystal C is obtained by subtracting the extrapolated extrinsic conductivities from the observed conductivities. After this subtraction was made, crystal C gave only one intrinsic region, which was almost identical to that of A and B.

The mechanism for the intrinsic conductivity of an "absolutely pure" crystal of calcium or strontium fluoride seems to be, therefore, the thermal formation of fluorine ion interstitials and vacancies in equal quantities and the predominant migration of the fluorine ion vacancies.

The formation energies of these defects, calculated from equation (3), were (1) calcium fluoride, 60.0 kilocalories, and (2) strontium fluoride, 51 kilocalories. These energies compare favorably with those values obtained from Ure's data for calcium fluoride. For example, Ure had assumed a migration energy of 12 kilocalories and calculated a formation energy of 65 kilocalories (ref. 5). From Ure's data, however, a formation energy of about 58 kilocalories is obtained if a migration energy of 16 kilocalories is assumed. Finally, it is of considerable interest to compare these formation energies with a theoretical calculation by Franklin for calcium fluoride (ref. 16). Although several approximations were used in the calculations, an energy of 62 kilocalories was obtained, which is in excellent agreement with our results.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 20, 1966,
120-34-02-02-22.

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TABLE I. - ANALYSES OF THE CRYSTALS
IN MOLE PERCENT

Elements	Calcium fluoride (crystal A)	Strontium fluoride
Barium	0.14	0.7
Calcium	Major	.4
Magnesium	.1	.016
Strontium	(a)	Major
Potassium	.022	.13
Rubidium	.080	(a)
Sodium	.003	.012
Lanthanum	.1	(a)
Aluminum	.002	.003
Iron	.040	.036
Chromium	.028	.024
Cobalt	(a)	.040
Copper	.002	.020
Nickel	(a)	.013
Manganese	↓	.004
Hafnium		.015
Titanium		.003
Ruthenium	↓	.001
Phosphorus	.008	.010
Chloride	.006	.001

^aNot detected.

TABLE II. - ENERGY REQUIREMENTS FOR CRYSTALS OF STRONTIUM FLUORIDE
AND CALCIUM FLUORIDE FOR EXTRINSIC REGION

Crystal	Faceplane	Observed for extrinsic region	Calculated for impurity controlled extrinsic region	
		Energy of activation, K, kcal/mole	Preexponential factor, A _I , ohm ⁻¹ cm ⁻¹	Energy of activation, K _I , kcal/mole
SrF ₂	---	18.7	1.22±0.05×10 ⁻²	17.4±0.9
CaF ₂ (A)	111	17.0	1.11±0.01×10 ⁻¹	16.5±0.1
CaF ₂ (B)	110	17.1	1.21±0.01×10 ⁻¹	16.5±0.1
CaF ₂ (C)	100	12.2	8.0±0.5×10 ⁻³	12.1±0.1
CaF ₂ (A') ^a	110	----	-----	11.8
CaF ₂ (A'') ^b	111	----	-----	13(430 ^o to 470 ^o C) 17(470 ^o to 555 ^o C)

^aCrystal A turned to its 110 face.

^bCrystal A turned back to its original 111 face after observing as A'.

TABLE III. - ENERGY REQUIREMENTS FOR CRYSTALS OF STRONTIUM FLUORIDE
AND CALCIUM FLUORIDE FOR INTRINSIC REGION

Crystal	Faceplane	Observed for intrinsic region Energy of activation, E, kcal/mole	Calculated for pure material in intrinsic region		
			Energy of activation, E _P , kcal/mole	Preexponential factor, A _P , ohm ⁻¹ cm ⁻¹	Energy of activation, E _P , kcal/mole
				Best overall values	
SrF ₂	---	42.8±0.1	43.1±0.2	6.6±0.2×10 ⁵	43.1±0.2
CaF ₂ (A)	111	45.5±0.1	46.9±0.2	4.16±0.08×10 ⁶	46.5±0.3
CaF ₂ (B)	110	45.0±0.1	46.4±0.1	4.02±0.06×10 ⁶	46.5±0.2
CaF ₂ (C)	100	41.6±0.2	-----	-----	-----
		44.5±0.1	-----	-----	-----
CaF ₂ (C') ^a	100	44.9±0.2	-----	-----	-----
CaF ₂ ^b	---	-----	-----	4.08±0.10×10 ⁶	46.5±0.2

^aSubtract lower extrinsic region conductivity from intrinsic region conductivity of C.

^bCombination of crystals A and B.

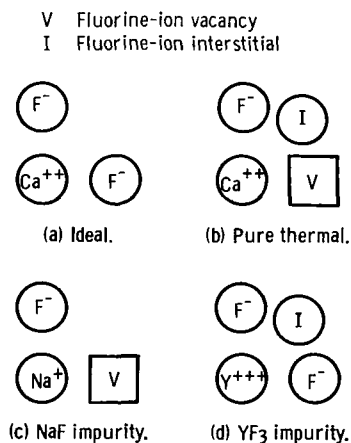


Figure 1. - Point defects in ideal, pure, and impure calcium or strontium fluoride.

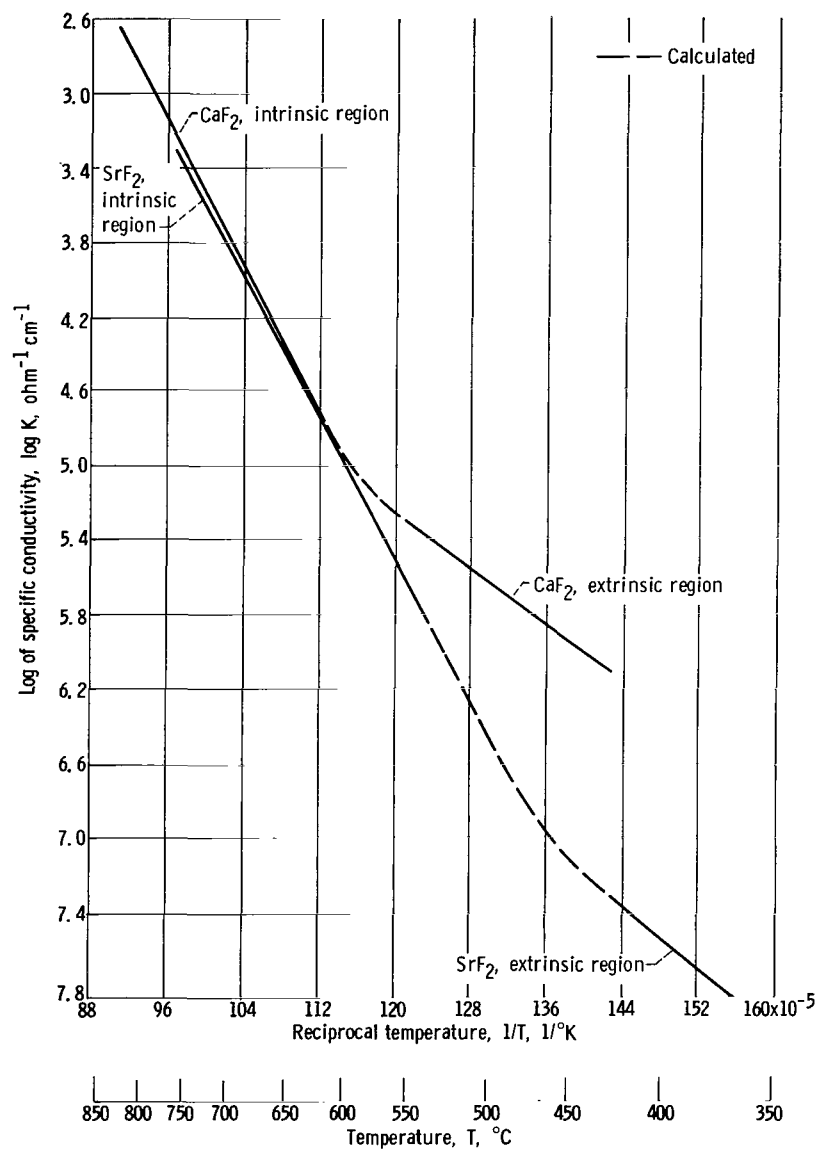


Figure 2. - Specific conductivity of single crystals of calcium and strontium fluoride.

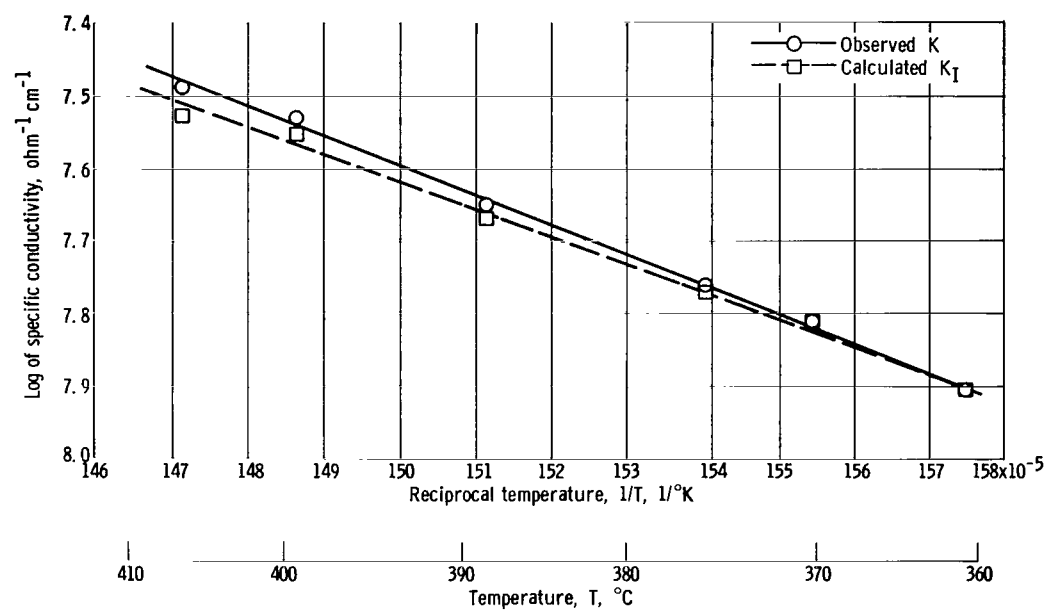


Figure 3. - Specific conductivity of strontium fluoride in extrinsic region.

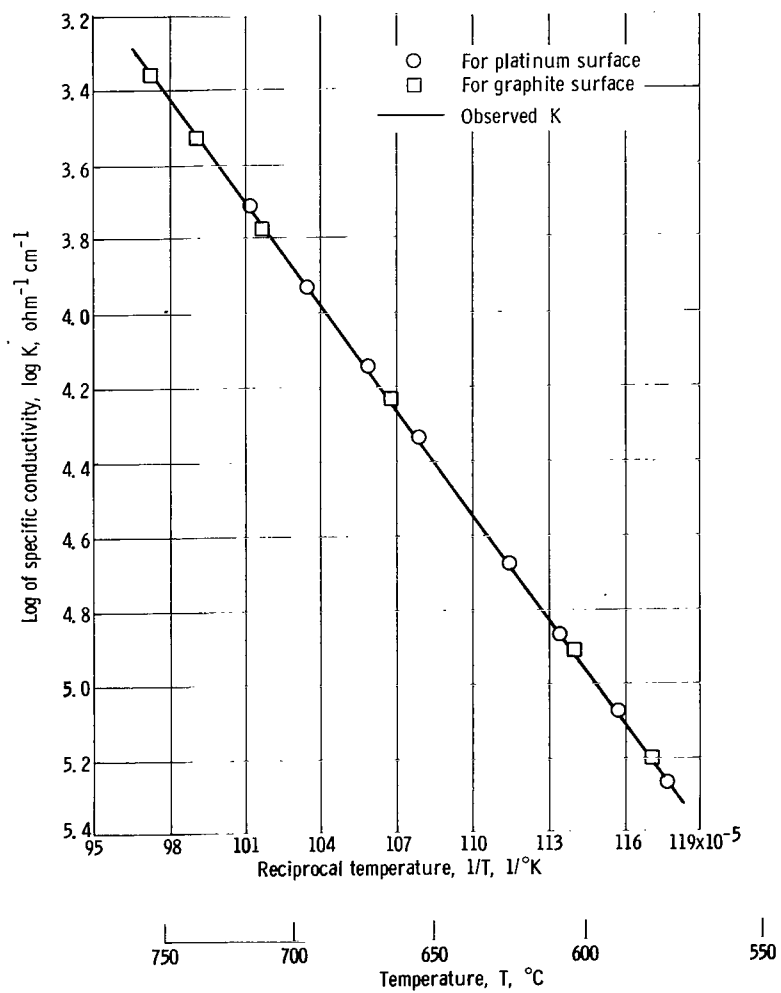


Figure 4. - Specific conductivity of strontium fluoride in intrinsic region at 1 kcps.

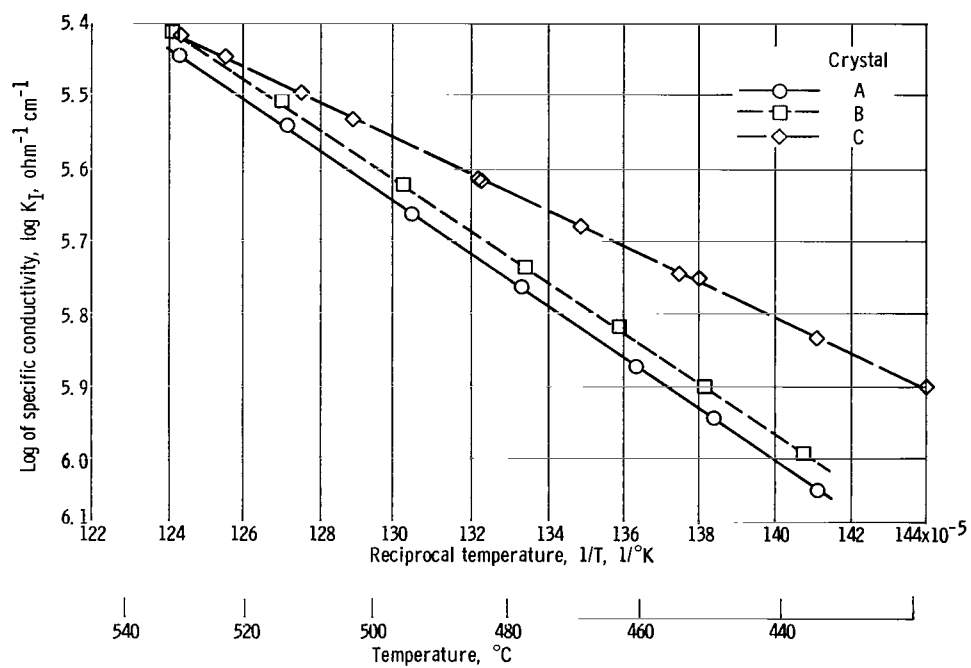


Figure 5. - Specific conductivities for calcium fluoride crystals (A, B, and C) for extrinsic region at 100 cps.

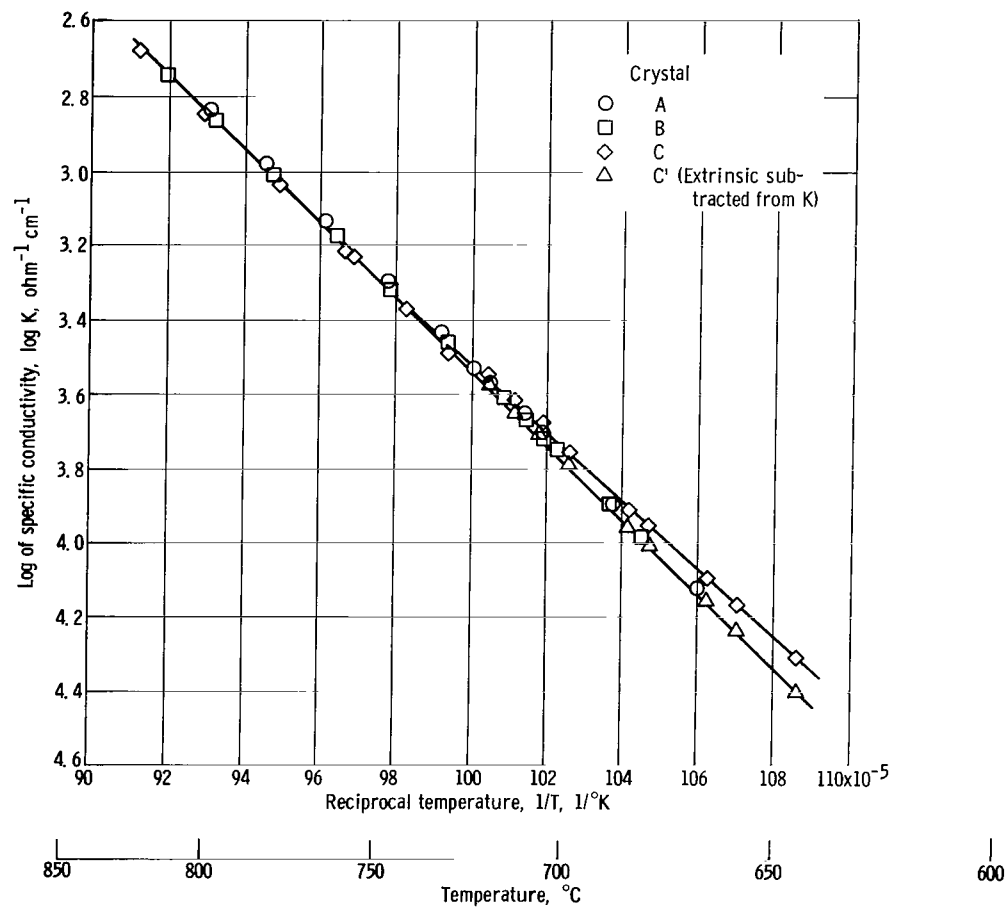


Figure 6. - Specific conductivity for calcium fluoride for intrinsic region at 1 kcps.

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